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Investigation of Product-Layer Diffusivity for CaO Sulfation

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16. ABSTRACT The paper gives results of comparisons of the sulfation rates of CaO prepared from Ca(OH)2 and CaCO3, using six types of each precursor derived from the same natural limestones. The particles were small enough to eliminate all transport resistances except diffusion through the CaSO4 product layer. No significant difference between the reactivity of the two types of CaO was observed when compared at equal values of specific surface area (23 sq m/g), temperature (800 C), and SO2 partial pressure (304 Pa). The apparent product-layer diffusivity at these conditions was 2.1 x 10 to the minus 8th power sq cm/sec. For an activation energy of 33 kcal/mol, the Arrhenius pre-exponential factor for diffusion is estimated to be 0.12 sq cm/sec. Sulfation rates increased with the 0.64 power of SO2 partial pressure. Comparison of the limestone-derived CaO with material prepared from pure CaCO3 showed lower reaction rate and lower calculated diffusivity for the pure CaO. The observed effects are in qualitative agreement with the hypothesis that diffusion occurs by a solid state mechanism.

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Sulfur Dioxide		

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An Investigation of Product-Layer Diffusivity for CaO Sulfation

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The sulfation rates of CaO prepared from $Ca(OH)_2$ and $CaCO_3$ were compared using six types of each precursor derived from the same natural limestones. The particles were sufficiently small to eliminate all transport resistances except diffusion through the $CaSO_4$ product layer. No significant difference between the reactivity of the two types of CaO was observed when compared at equal values of specific surface area (23 m^2/g), temperature (800 °C), and SO_2 partial pressure (304 Pa). The apparent product-layer diffusivity at these conditions was 2.1×10^{-8} cm^2/s. For an activation energy of 33 kcal/mol, the Arrhenius preexponential factor for diffusion is estimated to be 0.12 cm^2/s. Sulfation rates increased with the 0.64 power of SO_2 partial pressure. Comparison of the limestone-derived CaO with material prepared from pure $CaCO_3$ showed lower reaction rate and lower calculated diffusivity for the pure CaO. The observed effects are in qualitative agreement with the hypothesis that diffusion occurs by a solid-state mechanism.

Calcination of a $CaCO_3$ particle, initially nonporous, yields a CaO particle of the same dimensions with 54% of its volume as free pore space. Similarly, the calcination of a nonporous $Ca(OH)_2$ particle yields CaO with 49% porosity. The resulting calcines can be regarded either as an assemblage of nonporous CaO grains surrounded by intergranular voids or as a solid continuum that is randomly penetrated by pores. When such particles react with a gas, the rate of reaction is influenced by two principal processes: diffusion of the gas through the intergranular voids (or pore structure) and reaction at the grain (or pore) surface. The latter process may be dominated by chemical or by product-layer-diffusion steps.

At a given temperature, the relative resistance of pore diffusion decreases with the size of the CaO particle. Sulfation rate measurements made on CaO particles small enough to eliminate their pore diffusion resistance have shown (Borgwardt and Bruce, 1986) that the conversion vs. time data follow a response indicative of product-layer-diffusion control:

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = k_d t \qquad (1)$$

This conclusion was substantiated by experiments that varied the specific surface area of the CaO. Measurements of the time required to reach a given value of conversion ($X = 0.2$) at a given temperature and SO_2 partial pressure decreased with the square of the initial surface area in accordance with eq 1 and the expectation that

$$k_d = \frac{2\rho M D_e C_g S_g^2}{3} \qquad (2)$$

when the reaction is controlled by diffusion through the $CaSO_4$ surrounding the individual CaO grains (assumed to be spherical) that comprise the porous particle.

The conclusion that this reaction is controlled by diffusion in the product layer was also reached by Sotirchos and Yu (1985) from an analysis of earlier experimental data that did not include the surface area effect. Using a random-pore structural model, they showed that knowledge of the diffusivity, D_e, in the $CaSO_4$ is sufficient for analysis and mathematical modeling of CaO sulfation. The usefulness of such models for engineering purposes is dependent on the accuracy of available estimates of D_e. A current example where a reliable sulfation model is needed is the proposed process for reducing SO_2 emissions from coal-fired power plants by injecting limestone or $Ca(OH)_2$ into the furnace.

Because of its industrial importance, the CaO sulfation reaction has been the subject of extensive research, some of which has included estimates of D_e and its Arrhenius temperature dependence:

$$D_e = D_0 e^{-E/RT} \qquad (3)$$

As indicated in Table I, the reported values of the activation energy, E, show reasonable agreement. These values have been normalized on a partial pressure basis, employing the most recent estimate of the relationship between C_g and p_{SO_2} (Borgwardt and Bruce, 1986) to avoid the assumption that C_g equals the bulk gas concentration. The effect of p_{SO_2} is further examined in this paper.

One can conclude from Table I that E has a value of 33 ± 3 kcal/mol on the p_{SO_2} basis. The value of the other parameter required to define the diffusivity is far less clear, however, as indicated by Table II—estimates of D_0 obtained from published D_e values range over 2 orders of magnitude. With such uncertainty regarding D_0, efforts to formulate a model to predict process performance will not be successful. From the practical standpoint, the problem requires answers to the following questions: Can the discrepancies be explained by inherent variations in reactivity of samples from different sources, or are they due to errors introduced by the different methods of quantifying the pore diffusion effects which had to be factored out of the data to obtain D_e? If one cannot assume an intrinsic diffusivity for the $CaSO_4$ produced during sulfation of naturally occurring materials, what are the limits of variation attributable to the type of CaO precursor and its impurities?

From the fundamental standpoint, the observed effect of impurities on D_e has important implications regarding transport mechanism. Recent experimental investigations of this, and related, gas–CaO reaction (Hartman and Trnka, 1980; Bhatia and Perlmutter, 1981) suggest that the diffusion process involves ion transport rather than gas transport. If this hypothesis is correct, pure CaO should

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Table I. Activation Energy for CaO Sulfation

investigator	conversion range, %	temp range, °C	particle size, μm	E, kcal/mol	
				concn basis	p_{SO_2} basis[a]
Pigford and Sliger, 1973	1.4–11	871–1007	90	30	28.6
Ishihara and Hukuzawa, 1975	15–20	850–1000	3.4–12		35[b]
James and Hughes, 1976	2–25	800–1075	70	31	29.6
Hartman and Trnka, 1980	36	800–950	565	34	32.5
Marsh and Ulrichson, 1982	8	841–932	<50	35.6	34
Bhatia and Perlmutter, 1983	4–60	650–980	95	25.8	24.6[c]
Bardakci, 1984	0	755–942	single disk	34.1	32.6
Borgwardt and Bruce, 1986	10–60	800–1125	1		36.6

[a] Concentration data normalized with $C_s \propto (p_{SO_2})^{0.62}$. [b] Average of five runs, pilot furnace injection. [c] Includes data below equilibrium for $CaSO_3$ formation, E = 33 kcal/mol for high-temperature data.

Table II. Product-Layer Diffusivity for CaO Sulfation

investigators	temp, °C	$10^3 D_m$, cm^2/s	D_p, cm^2/s[a]
Hartman and Coughlin, 1976	850	0.6	0.017[b]
Georgakis et al., 1979	850	0.8	0.022[c]
Georgakis et al., 1979	980	250	1.50
Hartman and Trnka, 1980	850	5.5	0.15
Bhatia and Perlmutter, 1981	850	0.86	0.024[c]
Marsh and Ulrichson, 1982	841	11	0.35[b]
Bhatia and Perlmutter, 1983	870	16.7	0.36[d]
Christman and Edgar, 1983	815	4.0	0.18
Bardakci, 1984	840	0.08	0.0026[b]

[a] Calculated with E = 33 kcal/mol by eq 3. [b] Product layer expansion not accounted for. [c] Calculated from Hartman and Coughlin (1976) data. [d] Data from calcined dolomite.

be less reactive than CaO derived from limestones which contain foreign ions as natural impurities. Proof of this mechanism would bring many such reactions under the purview of the theory developed over the past 5 decades for ion transport in solids (Berniere and Catlow, 1983; Murch and Nowick, 1984). That framework has, for example, proved essential to understanding reactions involving the high-temperature oxidation of metals (Rapp, 1983).

Experimental Section

To eliminate pore diffusion effects, and thereby obtain measurements of sulfation rate limited only by product layer diffusion, particles smaller than 5 μm were used. The particles were calcined and exposed to $SO_2 + O_2$ in the differential reactor previously described (Borgwardt et al., 1984, 1986; Borgwardt and Bruce, 1986) at conditions that also eliminate interparticle diffusion resistance and permit control of the CaO specific surface area. The sample size used for each SO_2 reaction was 11 mg, dispersed in a quartz wool substrate through which the gas feed passed at 23 std L/min.

Two CaO precursors were examined: $CaCO_3$ and $Ca(OH)_2$. Six disparate limestones, containing a broad range of impurity concentrations (Table III), were the starting materials. The reactivity of CaO prepared from these stones was determined at fixed conditions of calcination and SO_2 exposure. Hydroxides prepared from the same calcined limestones were then evaluated. Finally, the diffusivities estimated from these rates were compared with those obtained from the sulfation of CaO prepared from chemically pure materials—a comparison that, surprisingly, has not been made in prior investigations.

The purposes of comparing the limestones with their hydroxide derivatives are as follows.

The first purpose is to test for a difference in CaO reactivity attributable to precursor type ($CaCO_3$ or $Ca(OH)_2$) when both contain the same impurities. Improved performance of the pollution control process when injecting hydroxides in furnaces cannot be currently explained.

Table III. Principal Impurities in Limestones Examined

limestone	wt %				
	Mg	Si	Al	Fe	total
Georgia marble	0.56	1.59	0.51	0.32	3.0
Vicron marble	0.21	0.93	0.16	0.0	1.3
Fredonia	0.27	0.60	0.069	0.16	1.1
Tate	0.90	1.94	0.53	0.09	3.5
Sylacauga	0.30	0.50	0.51	0.0	1.3
Whitestone	4.2	2.64	1.25	0.92	9.0

The second purpose is (for the hydroxides) to minimize the effect of nonimpurity-related defects (e.g., crystalline dislocations and associated stress) by means of (1) high-temperature annealing of the CaO prior to hydration and (2) structural rearrangements resulting from the conversion of CaO to $Ca(OH)_2$ and back again. The comparison should therefore indicate the importance of impurities relative to other factors influencing reactivity.

The third purpose is to obtain precursors (the hydroxides) that were prepared by a standardized procedure and with physical properties independent of geological history.

The fourth purpose is to provide checks on the individual D_s measurements.

All sulfation rates were measured at 800 °C. The reasons for this choice were (1) to maintain the temperature sufficiently low to control the critical variable—specific surface area—which is reduced by sintering (i.e., pore or grain growth) at a rate that accelerates with temperature, (2) to avoid loss of CaO porosity by particle shrinkage which can occur at high temperature, and (3) to avoid $CaSO_3$ formation which is thermodynamically favorable below 760 °C.

Surface areas were adjusted to the maximum range anticipated for the furnace injection process (20–25 m^2/g of CaO). This adjustment was complicated by the fact that $CaCO_3$ samples yielded CaO of higher specific surface area than the $Ca(OH)_2$ when both were calcined at 800 °C. The difference is explained by the lower decomposition temperature of the hydroxide, which was completely converted to CaO during the 2-min heatup period: the sintering process begins immediately when CaO is formed and is catalyzed by the released H_2O gas (Anderson et al., 1965) which remains in contact with the pore surfaces during the heatup period. $CaCO_3$ decomposed only 8% at the same conditions, and the released CO_2 quenches further decomposition at 800 °C. Consequently, the limestone and $CaCO_3$ samples were calcined at a higher temperature (880 °C). Other than calcination temperature, the same procedure was used to prepare CaO from both precursors: 2-min heatup, 75-s calcination at 23 std L/min flow of N_2, and 10-min sinter without flow.

The hydroxides were prepared by calcining 3 g of each limestone or $CaCO_3$ at 980 °C and annealing 90 min in a Pt crucible by using a N_2-purged muffle furnace. The resulting CaO (S_g = 3 m^2/g) was slaked in 10 mL of water

Table IV. Evaluation of Pore Structure Parameter for Equation 4

assumed ψ	sum of abs dev of eq from measd X values fraction conversion: S_g, m^2/g[a] 63	25	21	11.5	2.1	all S_g's
2.5	0.171	0.214	0.051	0.097	0.054	0.587
2.0	0.156	0.196	0.048	0.094	0.054	0.548
1.5	0.151	0.177	0.047	0.091	0.053	0.519
1.2	0.151	0.162	0.046	0.088	0.053	0.500
no. of data	12	12	6	7	8	45

[a] All calcines prepared from Fredonia limestone.

at 95 °C and the $Ca(OH)_2$ dried under flowing N_2 and repulverized. Microscopic examination showed particles uniformly about 3 μm in diameter, but the large specific surface areas (45 m^2/g) indicate these were agglomerates of much smaller crystals. The characterization is supported by nitrogen porosity measurements which showed 30% porosity in the high-surface hydroxide, 15% in commercial hydroxide, and 2% in limestone. TGA analyses confirmed that decomposition of the $CaCO_3$ to CaO and hydration of the CaO to $Ca(OH)_2$ were complete.

Evaluation of Diffusivity

Equation 2 does not account for expansion of the reacting CaO grains that occurs as sulfation progresses, an expansion caused by the larger molar volume of $CaSO_4$ relative to CaO. Equation 2 would thus yield estimates of D_s significantly lower than the true value. The random pore model formulated by Bhatia and Perlmutter (1981, 1983), which does account for product layer expansion, was therefore used to evaluate D_s from the X vs. t data. For the case where the rate is controlled by product layer diffusion, that model is

$$\left\{\frac{1}{\psi}[[1 - \psi \ln (1 - X)]^{1/2} - 1]\right\}^2 = k_r t \qquad (4)$$

where

$$k_r = \frac{MD_sC_sS_0^2}{2\rho Z(1 - \epsilon_0)^2} \qquad (5)$$

and

$$S_0 = \rho(1 - \epsilon_0)S_g = \rho_b S_g$$

$$Z = V_{CaSO_4}/V_{CaO}$$

$$\psi = \frac{4\pi L_0(1 - \epsilon_0)}{S_0^2}$$

Equations 4 and 5 show that the random pore model, like the grain model (eq 1 and 2), predicts that the time required to reach a given conversion decreases with the square of the surface area. The two models also predict similar shapes for the X vs. t response, as indicated by the comparison in Figure 1, up to conversions approaching the maximum (X = 0.57 for Z = 3.09) permitted by the available pore volume.

The values of the pore-structure parameter, ψ, used for Figure 1 bracket the measured values reported in the literature which range from 1.2 to 2.5. Since the particle size examined here is too small to permit direct measurement of ψ by mercury porosimetry, and because it cannot be assumed to be invariant with calcination conditions, ψ was evaluated by fitting eq 4 to X vs. t data for five limestone calcines prepared at varied temperatures (and times) to yield a broad range of surface areas. Table IV summarizes the results of this procedure. Minimum deviation of the data from eq 4 was obtained (within the experimentally verified range of ψ) with ψ = 1.2, which was used for all subsequent calculations. With this value of ψ, the random pore model provides a better correlation of the X vs. t responses than eq 1, which yields a total deviation of 0.547 when fit to the same five sets of data. The sulfation data used to evaluate ψ covered a range of conversion from 5% to 45% at 800 °C.

Table V. Product-Layer-Diffusivity Measurements with Limestone-Derived CaO at 800 °C, 304-Pa SO_2

CaO precursor	S_g, m^2/g uncalcined	calcined	$10^4 k_r$, s^{-1}	$10^9 D_s$, cm^2/s
Georgia marble	6.8	20.3	1480	3.22
		22.1		
Vicron marble	8.5	26.1	900	1.25
		26.7		
		26.8		
Fredonia limestone[a]	4.5			2.69[a]
Tate limestone	0.7	20.5	864	2.00
		21.9		
		19.1		
Sylacauga limestone	3.6	24.4	887	1.52
		23.4		
Whitestone limestone	0.9	17.5	735	2.11
		20.6		
		22.2 av		2.13 av

[a] From data of Borgwardt and Bruce (1986); D_s = 2.97 at S_g = 25 m^2/g, and D_s = 2.40 at S_g = 21 m^2/g.

Table VI. Product-Layer-Diffusivity Measurements with Hydroxide-Derived CaO at 800 °C, 304-Pa SO_2

CaO precursor	S_g, m^2/g uncal-cined	calcined	$10^4 k_r$, s^{-1}	$10^9 D_s$, cm^2/s
hydrated Georgia marble	44.7	23.0	1520	2.68
		23.9		
hydrated Vicron marble	47.7	24.1	700	1.38
		23.0		
hydrated Fredonia limestone	49.2	22.0	1080	2.08
	42.0	23.0		
hydrated Tate limestone	28.3	20.0	840	1.58
	29.0	25.5		
hydrated Sylacauga limestone	48.0	27.0	1580	2.22
		25.6		
hydrated Whitestone limestone	34.0	23.0	1200	2.21
		23.4 av		2.03 av

In a like manner, the value of k_r was determined for each CaO sample by fitting the X vs. t data to the left-hand side of eq 4 to minimize total deviation. The measurements were made at constant oxygen partial pressure of 5.07 kPa and 304 Pa of SO_2 in N_2 except where otherwise noted. The diffusivity was calculated from eq 5 using S_g values measured by N_2 adsorption with the multipoint BET method and M = 56 g of CaO/mol, $C_s = 3.41 \times 10^{-6}$ g-mol of SO_2/cm^3 (304 Pa at 800 °C), ρ = 3.32 g of CaO/cm^3, ϵ_0 = 0.54 for CaO derived from $CaCO_3$, ϵ_0 = 0.49 for CaO derived from $Ca(OH)_2$, Z = 3.09, and ψ = 1.2.

Results

Figure 2 shows conversion vs. time responses resulting from the sulfation of CaO derived from limestone and $CaCO_3$. Responses obtained with CaO prepared from $Ca(OH)_2$ are given in Figures 3 and 4. The curves are eq 4 with k_r values determined by best fit up to 45% conversion. Diffusivities calculated from the k_r values are summarized in Table V for the limestones and in Table

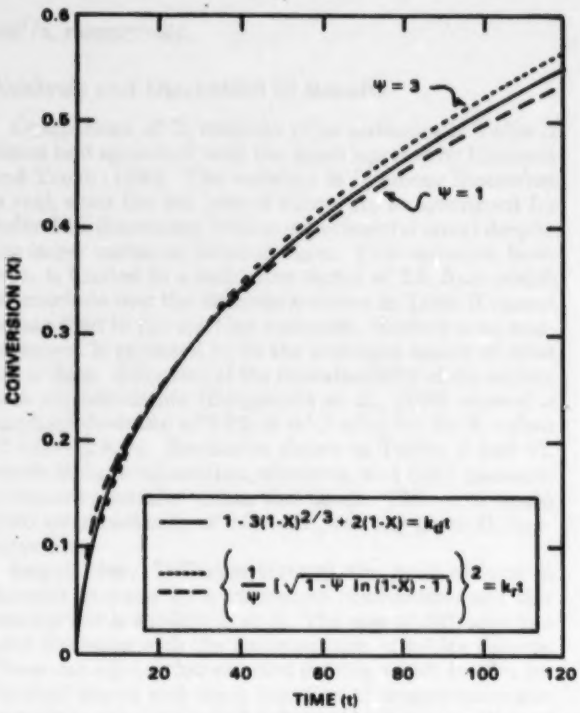

Figure 1. Comparison of relative responses predicted by grain model and random pore model for product-layer diffusion control.

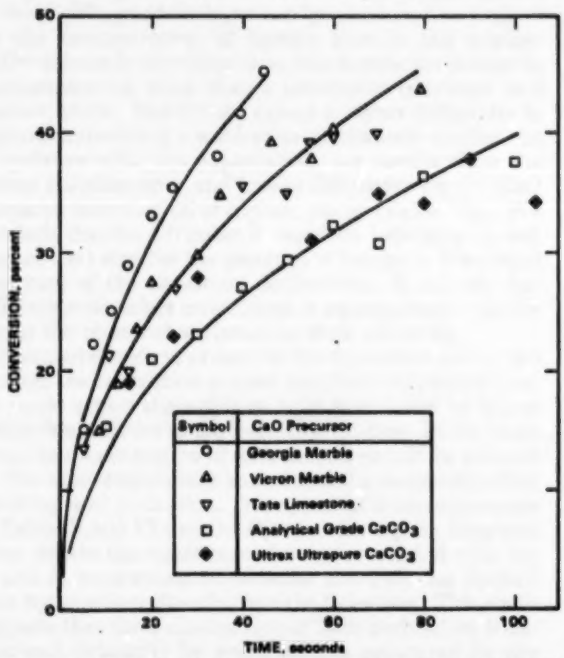

Figure 2. Reaction of limestone- and $CaCO_3$-derived CaO with 304-Pa SO_2 at 800 °C.

VI for their hydroxides. The average of six D_s measurements on limestone-derived CaO is 2.13×10^{-8} cm²/s, which is not significantly different from the average value obtained with the six hydroxides. The mean value of D_0 calculated by eq 3 from the combined measurements on both precursors (and $E = 33$ kcal/mol) is $D_0 = 0.118$ cm²/s.

Table VII gives the diffusivities determined for "pure" materials prepared from analytical grade $CaCO_3$ (Fisher

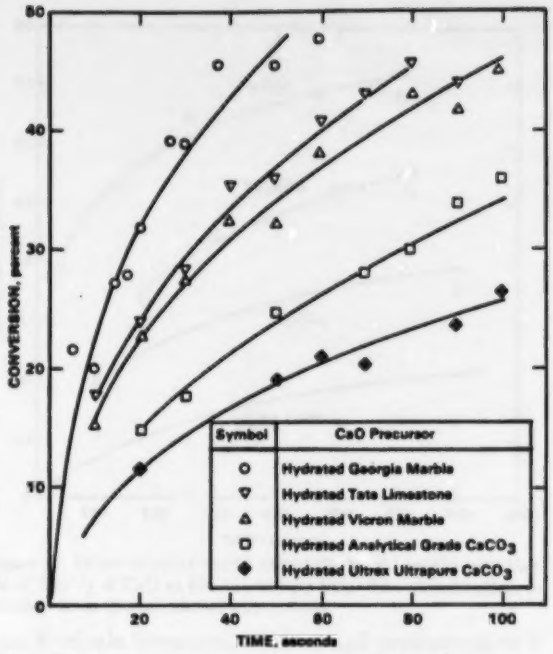

Figure 3. Reaction of $Ca(OH)_2$-derived CaO with 304-Pa SO_2 at 800 °C.

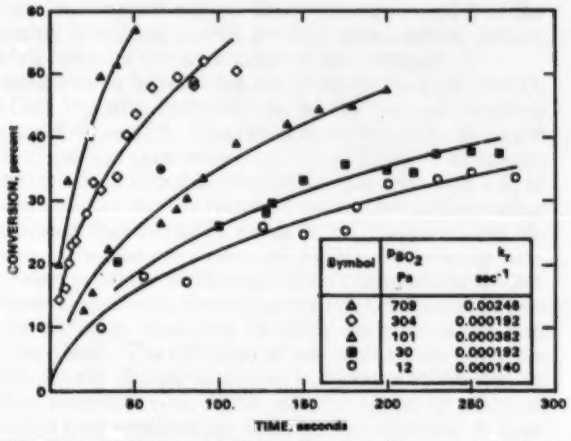

Figure 4. Sulfation of hydrated Fredonia limestone at 800 °C.

Table VII. Product-Layer-Diffusivity Measurements with Pure CaO

CaO precursor	S_g, m²/g: uncalcined	S_g, m²/g: calcined	$10^8 k_r$, s⁻¹	$10^9 D_s$, cm²/s
Ultrex ultrapure $CaCO_3$	1.3	41.4	496	0.30
		42.5		
		35.8		
analytical grade $CaCO_3$	0.5	25.7	512	0.66
		28.9		
hydrated Ultrex ultrapure $CaCO_3$	15.9	23.6	190	0.33
hydrated analytical grade $CaCO_3$	11.2	19.0	320	0.74
	12.4	19.8		

Scientific Co.) and ultrapure $CaCO_3$ (J.T. Baker Chemical Co., Ultrex). In the latter, the total metallic and nonmetallic impurities are certified less than 200 ppm. These materials yielded D_s values of 0.7×10^{-8} and 0.3×10^{-8}

cm^2/s, respectively.

Analysis and Discussion of Results

Comparison of D_0 with the prior estimates in Table II shows best agreement with the result reported by Hartman and Trnka (1980). The variation in D_s among limestones is real, since the two sets of values are in agreement for individual limestones (within experimental error) despite the larger variation between them. This variation, however, is limited to a maximum factor of 2.6, from which we conclude that the differences shown in Table II cannot be ascribed to the starting materials. Surface area measurement is expected to be the principal source of error in our data. Estimates of the reproducibility of the surface area measurements (Borgwardt et al., 1986) showed a standard deviation of 7.6% or ± 1.7 m^2/g for the S_g values of interest here. Replicates shown in Tables V and VI, which include calcination, sintering, and BET measurement, are generally within that range. This error would yield an uncertainty of ± 0.5 cm^2/s in any given D_s measurement.

Impurities. Diffusion through the product layer is thought to occur by a solid-state mechanism, and this assumption is implicit in eq 3. The rate of diffusion in a solid increases with the concentration of lattice defects. These can exist either as point defects, which involve individual atoms and are a function of temperature and impurities, or as extended defects, which involve lines or planes of disorder in the crystal structure (West, 1984). At a given temperature, the concentration of point defects in the $CaSO_4$ product layer can be presumed to depend on the concentration of foreign ions in the original CaO—especially aliovalent ions, which generate defects to compensate for local charge imbalance (Berniere and Catlow, 1983). One should expect a higher diffusivity in impure materials if a solid-state mechanism applies. In accordance with this expectation, our results show the lowest reaction rates and lowest diffusivity for the CaO prepared from $CaCO_3$ of highest purity (Table VII). We conclude that the difference in reactivity between pure and impure CaO signifies the presence of defects in the crystal structure of the limestone derivatives. It follows that differences in defect concentration among stones contribute to the observed variation in their reactivity.

If extended defects present in the limestones are carried through the calcination process into their CaO derivatives, we would expect those defects to be manifested by higher diffusivities relative to the hydroxide calcines. In the latter case, the concentration of such defects should be reduced by the high-temperature anneal and the recrystallization resulting from hydration. It is apparent from comparison of Tables V and VI that the D_s values for a given limestone agree within the experimental error associated with the S_g and k_r measurements, whether the CaO was derived from hydroxide or directly from the limestone. This result suggests that the sulfation rate of both derivatives is determined primarily by point defects generated by the impurities—at least for the conditions of calcination and sintering used in these measurements.

Doping. The effect of aliovalent impurities is perhaps demonstrated more directly by Bardakci's experiment (1984) which showed that NaCl vapor added to the reactant gas stream increased the product layer diffusivity by an order of magnitude. We carried out similar experiments which also show faster sulfation when alkali metal ions are present on the surface of well-annealed CaO during its sulfation. In this case, the sulfate salt was added to the CaO by grinding in a mortar. (The CaO was prepared from 3-μm Fredonia limestone, calcined and presintered to 3 m^2/g.) The effect of this quasi-impurity on the sulfation reaction is shown in Figure 5. The results can be interpreted as enhancement of solid-state diffusion by foreign ions: single-valent cations that are incorporated into the growing (divalent) $CaSO_4$ product cause lattice defects which promote the movement of ions through it.

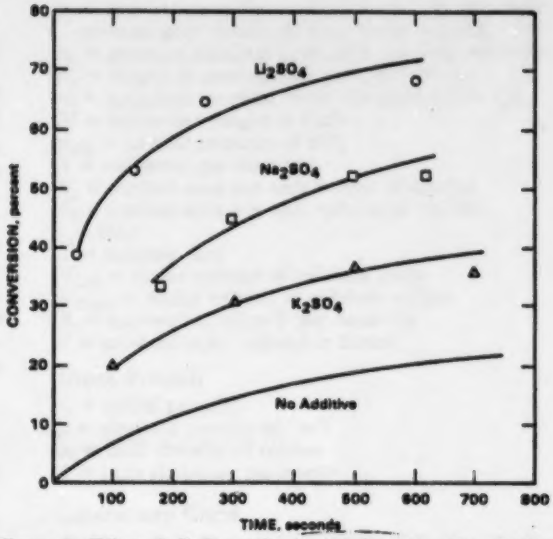

Figure 5. Effect of alkali-metal salts (9% by wt) on the sulfation rate of 3 m^2/g of CaO at 800 °C, 304-Pa SO_2. The added sulfate is excluded from the calculated conversions.

Attempts to increase the reactivity by "doping" $CaCO_3$ or $Ca(OH)_2$ with Na^+ prior to calcination and sintering were not successful. This result is explained by the rapid loss of surface area caused by the additive. The calcine prepared from doped hydroxide, for example, had a S_g of 1.4 m^2/g following the standard calcination and sintering treatment that normally yields 23 m^2/g without the additive. The observed effect of doping on sintering nevertheless provides additional indirect support for the ion diffusion hypothesis, since sintering kinetics are also known to be diffusion controlled in many cases (Goodson and White, 1962). The diffusion of ions which must occur for grain growth during sintering is likewise attributed to defect structure (Oel, 1962), and the observed effect of additives on accelerating that type of diffusion is thus ascribed to defects generated by aliovalent ions which enter the host lattice (Kriek et al., 1959; Layden and McQuarrie, 1959). The similarity of sintering and sulfation processes is therefore apparent, as is the probable mechanism underlying both. The analogy suggests that limestone and $CaCO_3$ calcines should show surface areas increasing with purity, a relationship that is evident in the data of Tables V and VII.

SO_2 Partial Pressure. To calculate D_s, two assumptions were necessary: (1) that Z is constant within the range of impurity concentrations studied and (2) that C_s equals the bulk gas concentration. The latter assumption is justified only if SO_2 is the diffusing species, which conflicts both with the observed activation energy of the diffusion step (33 kcal/mol) and with recent measurements of the effect of SO_2 partial pressure on the reactivity of $CaCO_3$-derived CaO in the absence of pore diffusion resistance (Borgwardt and Bruce, 1986). To examine this assumption for $Ca(OH)_2$-derived CaO, we evaluated the effect of p_{SO_2} on the reactivity of three hydroxides in the present study. Figure 4 summarizes the results for one of those, hydrated Fredonia limestone. k_r increases with p_{SO_2}

in the manner previously determined for $CaCO_3$ and

$$C_s = k_0(p_{SO_2})^m \quad (6)$$

where $m = 0.70$ for the data of Figure 4 and $m = 0.63$ and 0.65 for the other two hydroxides. Based on the combined results of these values, plus the three prior measurements with $CaCO_3$, we conclude that $m = 0.64 \pm 0.05$ and the calculated D_0 represents a lower limit on the true value. If the mechanism of transport through the product layer involves ionic diffusion rather than interstitial SO_3, C_s may denote either O^{2-} or SO_4^{2-}, and k_0 can depend on the rate of oxidation at the surface. Experiments with known catalysts of SO_2 oxidation (V_2O_5, Fe_2O_3) added in the manner of Figure 5 showed little effect on the CaO sulfation rate, indicating that the oxidation step was not limiting at those conditions.

Conclusions

The results show that a higher reactivity of $Ca(OH)_2$ relative to $CaCO_3$ cannot be attributed to intrinsic kinetics. The superior performance reported for hydroxide in boiler injection tests is best explained as a particle size effect: hydration of CaO expands the grains and breaks them to submicrometer-sized crystals, as evidenced by the order of magnitude increase in specific surface area of the raw sorbent. Although these crystals are fused into micrometer-sized agglomerates, they contain an inter-crystal pore structure that may allow access of SO_2 to the high-surface CaO generated within them when they decompose thermally.

Particles of such small size cannot be economically produced from limestone; fine grinding normally yields a distribution ranging from 1 to 100 μm. The larger particles will yield CaO that has strong pore diffusion resistance at the high temperatures (900–1200 °C) and high CaO surface areas required for efficient SO_2 capture in the short (1-s) residence time available in boiler furnaces.

The product layer diffusivity varied by a factor of 2.6 in the six relatively pure limestones examined; larger variations are probable in a broader range of materials. The differences are due primarily to point defects caused by impurities, which range in concentration, valence, and manner of incorporation in the $CaCO_3$ lattice. The hypothesis that diffusion occurs by an ionic mechanism, originally introduced to explain the high activation energy of this reaction, also provides a consistent basis for interpreting the effect of impurities on CaO sulfation and sintering.

Nomenclature

C_s = concentration of diffusing species at the product layer surface
D_0 = Arrhenius preexponential factor
D_s = product layer diffusivity
E = activation energy for diffusion
k_d = rate constant for product layer diffusion according to grain model
k_r = rate constant for product layer diffusion according to random pore model, defined by eq 4 and 5
k_0 = constant relating C_s to bulk-gas SO_2 concentration
L_0 = length of pore system per unit volume
m = apparent reaction order with respect to p_{SO_2}
M = molecular weight of CaO
p_{SO_2} = partial pressure of SO_2
R = universal gas constant
S_g = surface area per unit weight of calcine
S_0 = surface area per unit volume of calcine
t = time
T = temperature
V_{CaO} = molar volume of calcium oxide
V_{CaSO_4} = molar volume of calcium sulfate
X = conversion, atom S per atom Ca
Z = product-layer expansion factor

Greek Symbols

ϵ_0 = initial porosity
ρ = absolute density of CaO
ρ_b = bulk density of calcine
ψ = pore structure parameter

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